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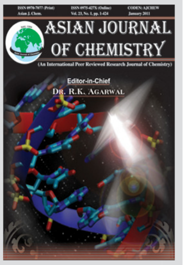

Solvent Extraction of Palladium(II) from Hydrochloric Acid Solution Using Octyl Benzothiazolyl Sulfide

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A new octyl benzothiazolyl sulfide (OBTS) was synthesized and used in the extraction of Pd(II) from hydrochloric acid solution. Pd(II) was extracted quantitatively with octyl benzothiazolyl sulfide in toluene. Thiourea solution could be used as stripping agent. Extraction parameters of Pd(II), including octyl benzothiazolyl sulfide concentration, palladium concentrations in the feed solution, contact time of aqueous and organic phases, organic/aqueous (O/A) phase ratio, thiourea concentration and H^+ concentration of aqueous phase, were studied in detail. IR analysis of Pd(II)-OBTS complex indicated that octyl benzothiazolyl sulfide coordinated with palladium *via* the thiazole N atom.

Key Words: Palladium, Solvent extraction, Octyl benzothiazolyl sulfide.

INTRODUCTION

Palladium has been widely used as catalysts in the automobile, chemical and petroleum industries. Palladium is also used as conductors in the electrical and electronic industries[1-5]. The primary resources of palladium is quite scarcity, leading to a limited supply available for industry. Therefore, efficient and selective extraction/separation of palladium is essential for the recycling of this metal from the secondary resources. The conventional method for the separation of palladium from other platinum group metals is by chemical precipitation. Precipitation process has inherent problems, such as high chemical consumption and high labour requirements involved in the repeated process, slow kinetics and solid-liquid separation[6]. The chemical precipitation process increases environmental pollution. The solvent extraction technique is one of the most versatile methods used for the removal, separation and concentration of palladium from mixed metal aqueous media[7-12]. Extraction reagents containing sulfur have been attracting much attention for their excellent extraction ability to palladium1[3-17].

In the present work, the behaviour of extraction of Pd(II) from hydrochloric acid solution with octyl benzothiazolyl sulfide has been studied, by controlling important parameters like extractant concentration, acidity, contact time, phase ratio and concentration of stripping agent.

EXPERIMENTAL

A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High-Technologies Corpotation, Japan) was used to measure the concentration of Pd(II). The operating conditions were carried out according to the recommendations of manufacturer. The wavelengths selected were as follows: Pd 247.6 nm. The pH values were measured with a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China).

Pd(II) stock solution (1.0 g L^{-1}): A weighed amount of palladium metal was dissolved in aqua regia (120 mL). When the metal was completely dissolved, the solution was evaporated to nearly dryness. Residual HNO_3 was removed by adding 30 mL of 6 mol L^{-1} HCl and evaporated to nearly dryness again and this was repeated 3 times. The solution was transferred into a 250 mL of volumetric flask and the final volume was adjusted by adding 0.1 mol L^{-1} HCl solution. The organic phases with desired extractant concentration were obtained by dissolving a definite volume of octyl benzothiazolyl sulfide (OBTS) in toluene.

Synthesis of octyl benzothiazolyl sulfide (OBTS): Octyl benzothiazolyl sulfide was synthesized according to the following procedure: 2-mercaptobenzothiazole (0.15 mol), acetone (150 mL) and KOH (0.18 mol) were put in a round-bottom fitted with a mechanical stirrer and condenser and the mixture was heated for about 0.5 h. 1-Bromooctane (0.15 mol) was then added gradually with stirring through a dropping funnel and the reaction mixture was refluxed for 6 h. The residual solid was filtered after cooling down and the acetone was removed by distillation. The organic phase was diluted with ether (20 mL), washed with water two times and dried with anhydrous Na_2SO_4. The ether was evaporated and OBTS was obtained. Its structure (Fig. 1) was verified by ^{1}H NMR, ^{13}C NMR and mass spectra. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz 1H), 7.68 (d, *J* = 7.75 Hz 1H), 7.35 (t, *J* = 7.6 Hz 1H), 7.22 (t, *J* = 7.1 Hz 1H), 3.30 (t, *J* = 7.4 Hz 2H), 1.80-1.76 (m, 2H), 1.44- 1.42 (m, 2H), 1.30-1.25 (m, 8H), 0.87 (t, *J* = 6.9 Hz 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.76, 153.84, 135.62, 126.37, 124.48, 121.87, 121.30, 34.03, 32.26, 29.66, 29.60, 29.53, 29.25, 23.12, 14.58 ppm; HRMS (ESI) m/z found (%): 280.1274 $(M + H)^+$; calcd. (%): 280.1188 $(M + H)^+$.

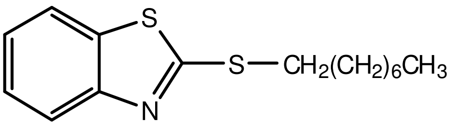

Fig. 1. Structure of octyl benzothiazolyl sulfide (OBTS)

General extraction procedure: Equal volumes (10 mL) of both phases were mixed and vigorously shaken for 0.5 h, which was sufficient enough to attain equilibrium in a preliminary experiment. After phase separation, the concentration of Pd(II) in aqueous solution was determined by an atomic absorption photometer. These results were further used to estimate the extraction efficiency of metal. The amount of extracted metal ion was calculated according to the differences in the metal concentrations of the aqueous phase between, before and after the extraction.

RESULTS AND DISCUSSION

Influences of the extractant concentration: To investigate the effect of octyl benzothiazolyl sulfide concentration on the extraction performances of Pd(II), the experiments were performed at the fixed conditions. The results are shown in Fig. 2. As can be seen from Fig. 2, OBTS dissolved in toluene with the extractant concentration varying from 1-9 % (v/v). The percentage extraction of Pd(II) increased in the range from 13.0-99.3 % by increasing octyl benzothiazolyl sulfide concentration from 1-7 % (v/v). Further increasing octyl benzothiazolyl sulfide concentration from 7-9 % (v/v), the percentage extraction of Pd(II) only had a slight increase (from 99.3-99.7 %). 7 % (v/v) OBTS was needed for quantitative extraction of Pd(II) from a 0.1 mol L^{-1} HCl aqueous solution containing 100 mg L^{-1} palladium.

Effect of metal ion concentration: Fig. 3 shows the effect of palladium concentration in the aqueous solution on the extraction of palladium. The percentage extraction of Pd(II) decreased in the range from 99.3-38.2 % by increase of palladium concentration in the aqueous phase from 0.1-1.0 g L^{-1}. Quantitative extraction of palladium was obtained in the range of 0.1-0.2 g L^{-1} palladium concentration in the aqueous phase. Therefore, 0.1 g L^{-1} palladium concentration in the aqueous phase was followed in all subsequent experiments.

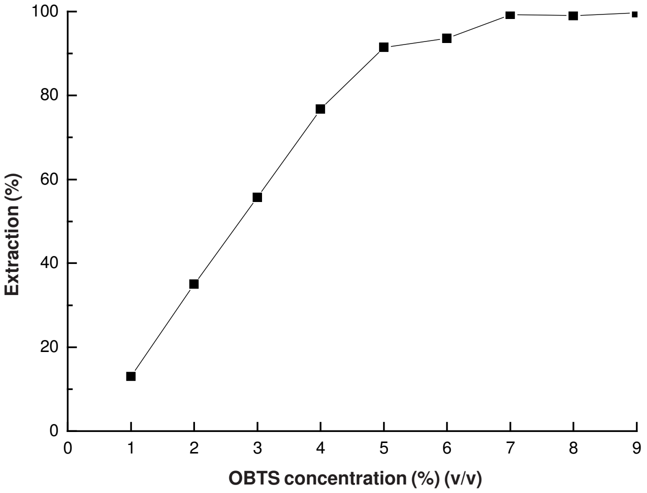

Fig. 2. Effect of extractant concentration on the extraction of Pd(II). $C_{Pd(II)}$: 100 mg L^{-1}, C_{HCl}: 0.1 mol L^{-1}, O/A: 1.0, contact time: 0.5 h

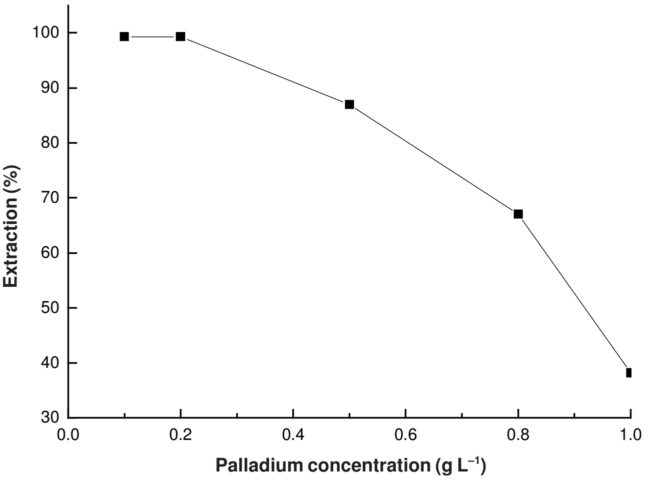

Fig. 3. Effect of palladium concentration on the extraction of Pd(II) C_{OBTS}: 7 % (v/v), C_{HCl}: 0.1 mol L^{-1}, O/A: 1.0, contact time: 0.5 h

Influences of concentration of H^+: In industrial application for extraction of Pd(II), the acidity of stock solution usually influences significantly. The effect of H^+ concentration on the extraction of Pd(II) is shown in Fig. 4. The extraction curve indicated the percentage of extraction of Pd(II) decreased drastically with the increase of H^+ concentration. The percentage extraction of Pd(II) decreased in the range from 99.3-24.2 % by increase of HCl concentration from 0.1-2.0 mol L^{-1}. Quantitative extraction of palladium occurred at 0.1 mol L^{-1} HCl. Therefore, 0.1 mol L^{-1} HCl was adopted in all subsequent experiments.

Influences of contact time: To extract Pd(II) efficiently by controlling an optimal contact time of aqueous and organic phases, the experiments were carried out with different contact time at other fixed extraction parameters. The results are shown in Fig. 5. Contact time was determined by measuring the metal content in the aqueous phase as a function of time until the metal concentration in the aqueous solution did not vary. The two phases were shaken for a period ranging from 5-35 min. The percentage extraction of Pd(II) increased in the range from 61.0-99.3 % by increasing contact time from 5-30 min. Further increasing contact time from 30-35 min, the percentage

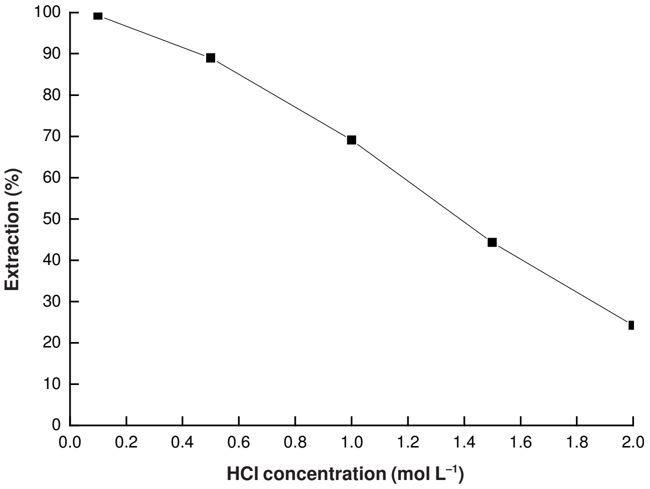

Fig. 4. Effect of HCl concentration on the extraction of Pd(II) $C_{Pd(II)}$: 100 mg L^{-1}, C_{OBTS}: 7 % (v/v), O/A: 1.0, contact time: 0.5 h

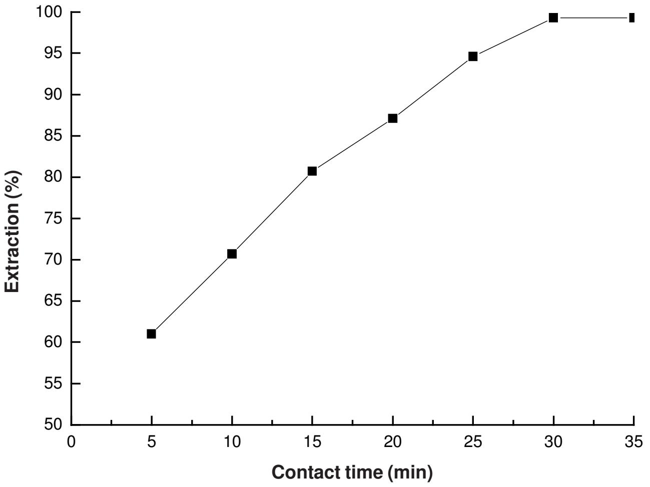

Fig. 5. Effect of contact time on the extraction of Pd(II) $C_{Pd(II)}$: 100 mg L^{-1}, C_{OBTS}: 7 % (v/v), O/A: 1.0, C_{HCl}: 0.1 mol L^{-1}

extraction of Pd(II) kept constant. Therefore, the minimum period of equilibration required for the quantitative extraction of palladium was found to be about 0.5 h.

Influences of organic/aqueous (O/A) phase ratio: To obtain optimal O/A for extraction of Pd(II), the following experiments were performed at other fixed extraction parameters. The results are shown in Fig. 6. As can be seen from Fig. 6, by increasing O/A from 0.4-1.0, the percentage extraction of Pd(II) increased from 98.2-99.3 %. By further increasing O/A from 1.0-1.2, the percentage extraction of Pd(II) kept constant. Therefore, Pd(II) can be extracted efficiently by controlling organic/aqueous (O/A) phase ratio, 1.0.

Stripping properties of palladium: Palladium loaded in the organic phase was stripped with various stripping agents, such as thiourea, hydrochloric acid, nitric acid, sodium hydroxide, ammonia and sodium sulfite as stripping agents. In the following experiments, the organic phase loaded with 100 mg L^{-1} Pd(II) was used. The experiments were carried out at the following fixed parameters: contact time of the two phases, 0.5 h; organic/aqueous (O/A) phase ratio, 1.0. The results show that palladium can not be stripped from organic phase with acid solution and sodium hydroxide. Thiourea solution can be used as an effective stripping agent. As can be seen from Fig. 7, by increasing thiourea concentration from 0.1-0.5 mol L^{-1}, the percentage stripping of Pd(II) increased from 56.3-99.7 %. By further increasing concentration of thiourea from 0.5-1.0 mol L^{-1}, the percentage stripping of Pd(II) kept constant. The stripping was quantitative when 0.5 mol L^{-1} thiourea solution was used.

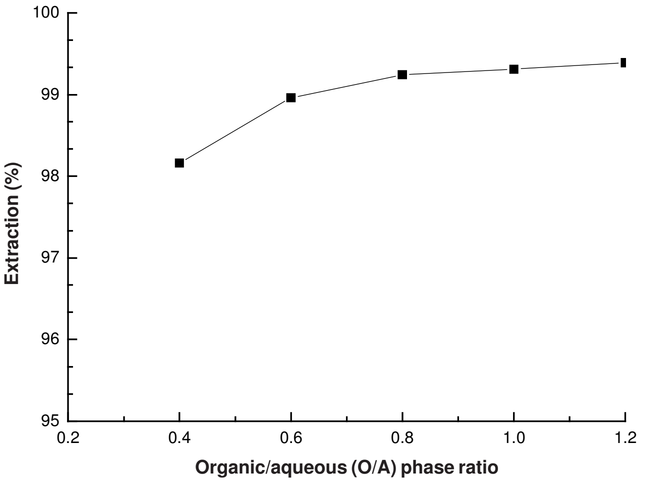

Fig. 6. Effect of O/A on the extraction of Pd(II). $C_{Pd(II)}$: 100 mg L^{-1}, C_{OBTS}: 7 % (v/v), contact time: 0.5 h, C_{HCl}: 0.1 mol L^{-1}

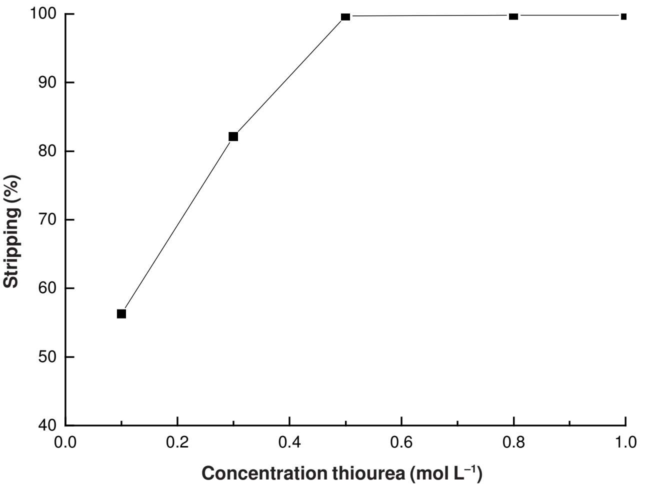

Fig. 7. Effect of stripping reagent concentration on the stripping of Pd(II). $C_{Pd(II)}$: 100 mg L^{-1}, C_{OBTS}: 7 % (v/v), O/A: 1.0, contact time: 0.5 h

IR spectra of extracted Pd(II)-OBTS complex: Fig. 8 shows the IR spectra of OBTS and Pd(II)-OBTS complex. The peak at 665 cm^{-1} attributed to the absorption of ν(C-S-C) of the benzothiazolyl ring[18] appears at 669 cm^{-1} in the Pd(II)-OBTS complex, indicating that the S atom is not coordinated with the metal ion. The C=N stretching vibration observed at 1636 cm^{-1} for OBTS is shifted to 1625 cm^{-1} in the Pd(II)-OBTS complex and the shift extent is similar to the Pd(II)-ABSO complex[14]. These facts indicated the OBTS is coordinated with Pd(II) *via* nitrogen atom on the thiazole ring.

Conclusion

The solvent extraction of Pd(II) from hydrochloric acid solutions were investigated using octyl benzothiazolyl sulfide (OBTS) diluted in toluene. Extraction parameters of Pd(II) were obtained and summarized as the following: octyl

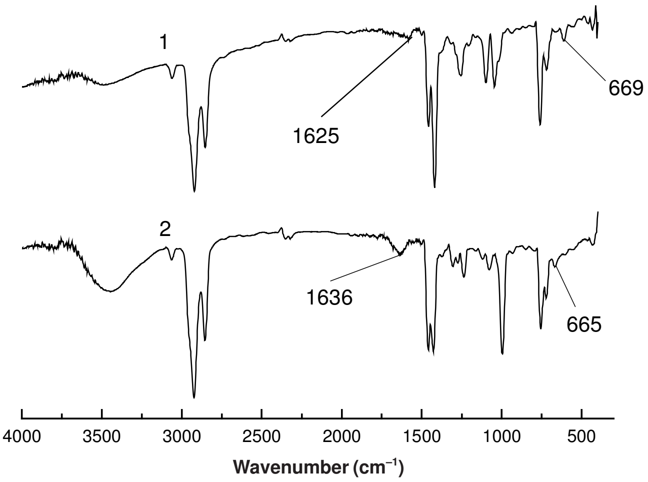

Fig. 8. Infrared spectra of Pd(II)-OBTS complex (1) and OBTS (2)

benzothiazolyl sulfide concentration, 7 % (v/v); organic/aqueous (O/A) phase ratio, 1.0; H^+ concentration of aqueous solution, 0.1 mol L^{-1}; contact time of two phases 0.5 h. Pd(II) loaded in organic phase could be stripped efficiently using an aqueous solution containing thiourea. IR analysis of Pd(II)-OBTS extraction adduct indicated that OBTS coordinated with palladium *via* the thiazole N atom, which is quite different from general alkyl sulfide which is coordinated with Pd(II) *via* S atoms of the ligands.

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